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TECHNICAL CONSIDERATIONS IN REGIONAL AEROSOL MODELING

by

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16. ABSTRACT

This work addresses the theoretical aspects of the behavior of aerosol particles in the atmosphere. In particular, it focuses on mathematical modeling of atmospheric aerosols at the regional scale (3001000 km). The paper discusses the evolution of the model in a stepwise fashion. First is considered the mathematical formulation of the transport mechanisms used. Second is a synopsis of the physical processes that affect aerosol dynamics of the aerosol population. Then, a review of the pertinent chemistry of atmospheric aerosols is given. Various mathematical models of aerosol dynamics and chemistry and the formulation of the complete aerosol model are discussed.

Concluding remarks include suggestions for future work such as the treatment of aerosols in clouds and model evaluation with data.

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INTRODUCTION

Particles that are emitted and formed in our atmosphere yield fumes, mist, and ashes. However, unlike the Greek mythological belief that a beautiful bird can be reborn from its ashes, the beauty of atmospheric ashes and particles appears only under certain angles when the light of Phebus can be directed advantageously by fine particles toward the human eye. Under other conditions, atmospheric particles adversely affect visibility by reducing visual range and delineating contrasting plumes. Fine particles are also inhaled by humans and may disturb the lung physiology when deposited in the tracheobronchial system. Moreover, the chemical species contained in these particles may disturb the ecological balance of our biota; for example, sulfate and nitrate particles that are deposited on the ground and on foliage acidify soils and watersheds.

A comprehensive approach to this variety of environmental issues requires an integrated study of atmospheric particles to assess their sources, evolution, and fate and to characterize their concentration, size

distribution, and chemical composition. Such a study must be both theoretical and experimental if our concepts of particle physics and chemistry are to be reconciled with our observations.

We address in this work the theoretical aspects of the behavior of aerosol particles in the atmosphere. In particular, we focus on the mathematical modeling of atmospheric aerosols at the regional scale. Previous modeling studies have concentrated on the simulation of aerosol dynamics in laboratory experiments, chimney plumes, or the stratosphere. No work has been performed so far on the mathematical description of aerosols in the lower layers of the atmosphere over distances of the order of 1000 km. Regional modeling is particularly important to the study of air pollution since pollutants can be transported over long distances and thus may have an environmental impact several thousands of kilometers downwind of the source. In addition, a regional model can also be used to calculate background conditions for urban-scale models. Such an endeavor requires us to consider a wide variety of physical and chemical processes that affect aerosols. To that end, we discuss in the following sections the formulation of a regional aerosol model.

We first provide a brief overview of the mathematical formulation of the transport mechanisms used in the regional model. Next, we provide an overview of the physical processes that affect the dynamics of the aerosol population. We then review the chemistry of atmospheric aerosols. Various mathematical models of aerosol dynamics and chemistry, and the formulation of the regional aerosol model are discussed before the presentation of concluding remarks.

OVERVIEW OF THE REGIONAL MODEL

The evolution of aerosol concentrations is treated at the regional scale by means of a three-dimensional gridded structure. Chemical reactions and aerosol dynamics take place within each grid cell. Advective and convective transport, dispersion, emissions of primary pollutants, and removal by dry deposition and sedimentation are treated as transport between grid cells.

The transport processes are treated by the regional model developed at the U.S. Environmental Protection Agency. The mathematical formulation of the model (Lamb, 1983), its computer implementation (Lamb, 1984a; Novak, 1984), and its preliminary application (Schere and Possiel, 1984) have been presented elsewhere. We therefore limit our discussion to a brief overview of the model formulation.

The EPA regional model is an Eulerian, grid-based, multiple-layer model that treats atmospheric processes relevant to the regional distribution of pollutants. The model includes three horizontal layers that vary spatially and temporally--the surface layer, the mixed layer, and the inversion, or cloud, layer. The model also includes a shallow surface layer adjacent to the ground for the treatment of surface processes such as dry deposition and near-ground chemical reactions. The vertical dimensions of the grid vary from 50 to 1000 m. The grid framework follows a latitude-longitude coordinate system with horizontal dimensions of the order of 18 km.

The EPA regional model treats such physical processes as horizontal transport including its nondeterministic aspects (Lamb, 1984b), nighttime wind shear, stability stratification, nocturnal jets, venting of pollutants from the mixed layer by cumulus clouds, mesoscale vertical motions induced by terrain and horizontal wind flow divergence, dry deposition, and emission of primary pollutants.

The EPA regional model also includes a chemical kinetic mechanism (CBM-X) that describes the chemistry of nitrogen oxides, anthropogenic and biogenic hydrocarbons, and photochemical oxidants such as ozone and hydrogen peroxide. This chemical kinetic mechanism currently includes 180 reactions and is based on a carbon-bond representation of hydrocarbon chemistry (Killus and Whitten, 1984). Gas-phase reactions for the chemistry of sulfur dioxide are included (Seigneur, et al., 1985). In its application to the regional aerosol model, the chemical kinetic mechanism must be condensed to fewer chemical species and reactions to allow the incorporation of additional variables describing the aerosol size

distribution and chemical composition. This condensation will be based on the results of a recent sensitivity analysis of the CBM-X (Gautier, 1984) that was carried out by means of a variational method (Seigneur et al., 1982).

AEROSOL DYNAMICS

The concentrations and sizes of aerosols are affected by a variety of dynamic processes including coagulation, growth and shrinkage, nucleation, sedimentation, dry deposition, and wet deposition. In this section we review the theoretical basis of these processes and assess their relevance to aerosol modeling at the regional scale.

Coagulation

Coagulation does not affect the total mass of aerosols because mass is conserved during the coagulation of two aerosols. However, coagulation affects the aerosol size distribution and aerosol total number concentration because it is the process by which two aerosols form one larger aerosol. Coagulation occurs via Brownian motion, sedimentation, and turbulent motion (e.g., Friedlander, 1977). In the atmosphere, Brownian motion is the most important mechanism for coagulation, as shown in Figure 1, where the coagulation coefficients are presented for various aerosol sizes. The change in the aerosol size distribution due to coagulation is represented mathematically as follows:

$$\frac{\partial n(v)}{\partial t} = \frac{1}{2} \int_0^v \beta(\tilde{v},\, v-\tilde{v})\; n(\tilde{v})\; n(v-\tilde{v})\; d\tilde{v} - \int_0^\infty \beta(v,\tilde{v})\; n(\tilde{v})\; n(v)\; d\tilde{v} \qquad (1)$$

where n(v) is the aerosol number distribution, v is the aerosol volume, and β is the coagulation coefficient. The coagulation rate decreases as the aerosol concentration decreases, i.e., coagulation affects the aerosol size distribution more in polluted air parcels such as stack plumes than

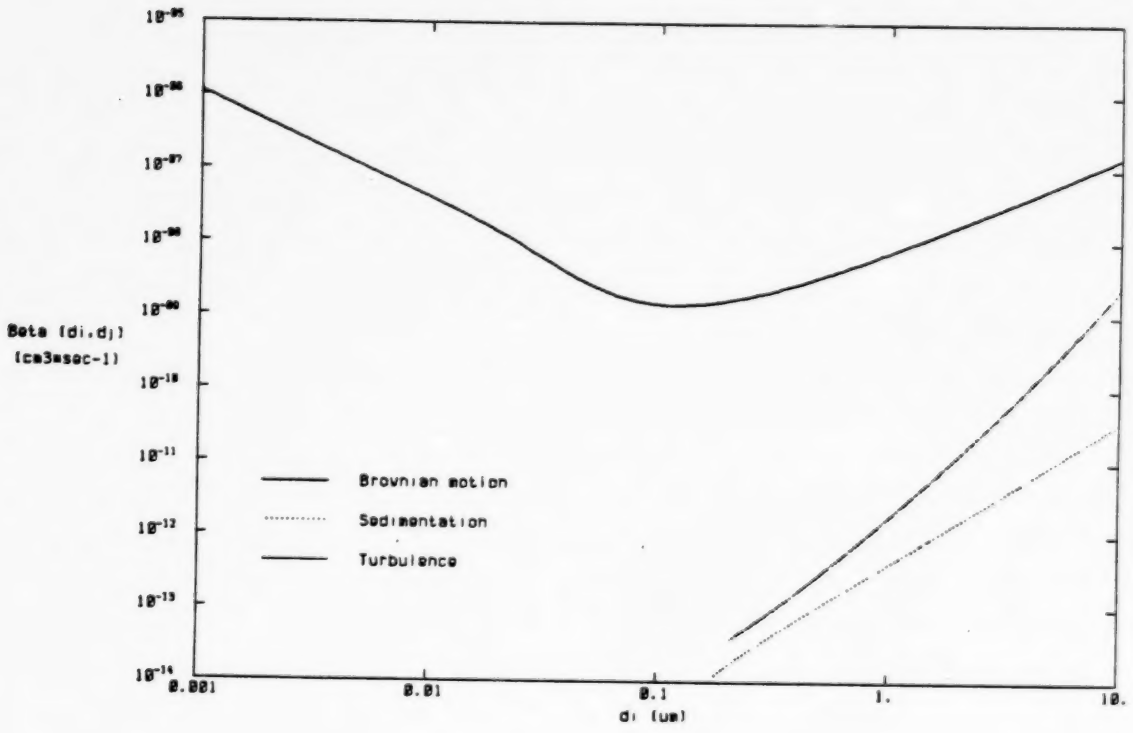

Fig. 1. Coagulation coefficients for an aerosol of 0.1 μm in diameter coagulating with aerosols in the 0.001 - 10 μm diameter range.

in cleaner areas such as pristine airsheds. It is therefore important to assess the contribution of coagulation at the regional scale, where aerosol concentrations are likely to be significantly lower than they are in a stack plume. To that end, we performed simulations of aerosol coagulation for aerosol concentrations typical of those observed at the regional scale.

The aerosol coagulation simulations were conducted by means of a sectional representation of the aerosol volume distribution (Gelbard et al., 1980; Seigneur, 1982). The simulations were conducted for 12 hours. Two initial aerosol size distributions were selected typical of hazy and urban atmospheres. The results of the simulations conducted with and without coagulation are presented in Figure 2. The initial size distributions do not change when coagulation does not occur. Coagulation appears to have a negligible effect in a hazy atmosphere, where the total aerosol volume below 2 μm is about 10 $\mu m^3 \cdot cm^{-3}$. In an urban atmosphere, where the total aerosol volume below 2 μm is about 44 $\mu m^3 \cdot cm^{-3}$, coagulation affects the concentrations of aerosols with diameters smaller than 1 μm, although the changes in aerosol concentrations are less than 10 percent for aerosols whose diameters are larger than 0.1 μm. However, to determine the necessity of including coagulation in aerosol regional modeling, one must also investigate the manner in which coagulation interacts with other dynamic processes such as aerosol growth.

Growth/Shrinkage

Aerosols may grow or shrink in size when material condenses or evaporates, respectively, or when its density changes due to a change in chemical composition. Growth or shrinkage does not affect the total aerosol number concentration; however, it affects the total aerosol mass and the aerosol size distribution. The change in the aerosol distribution due to growth or shrinkage of the aerosol is expressed mathematically as follows:

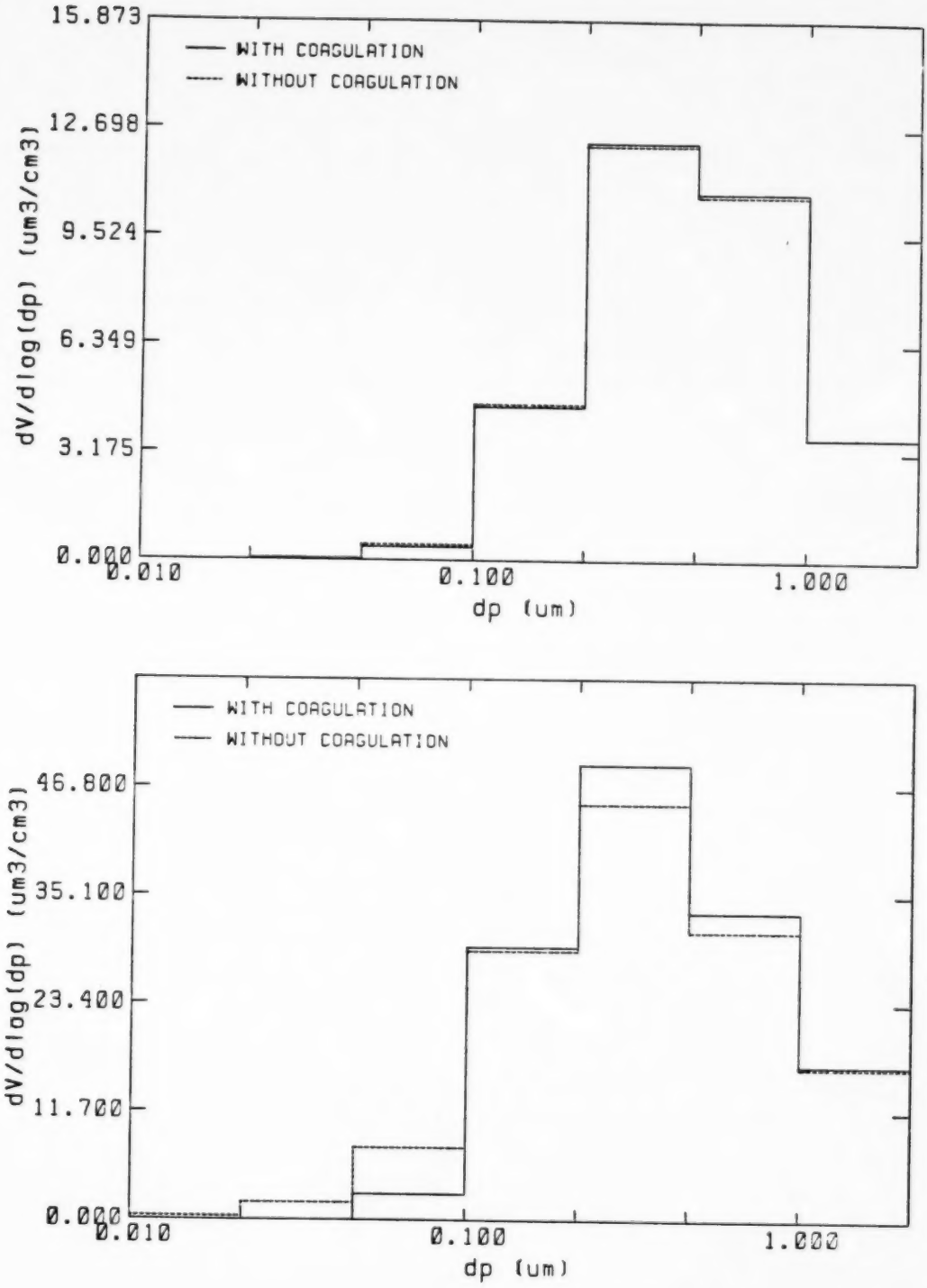

Fig. 2. Evolution of aerosol size distributions with and without coagulation for hazy (top) and urban (bottom) conditions.

$$\frac{\partial n(v)}{\partial t} = -\frac{\partial}{\partial v} n(v)\frac{dv}{dt} \qquad (2)$$

The growth/shrinkage rate of aerosols depends on their size, and this size dependence in turn depends on the chemical process leading to condensation/evaporation of aerosol material (e.g., Friedlander, 1977; McMurry, 1980; Seinfeld and Bassett, 1980).

Condensation may occur following the gas-phase formation of a condensible species such as H_2SO_4 (a diffusion-limited condensation process), the conversion of a volatile precursor to a condensed product via reaction at the aerosol surface (e.g., oxidation of SO_2 to H_2SO_4 at the surface of carbon soot particles) or in a liquid film coating the aerosol (e.g., aqueous oxidation of SO_2 to H_2SO_4 in the presence of trace metals), and the equilibrium redistribution of a volatile species such as HNO_3 or H_2O between the gas and aerosol phases (e.g., because of a change in temperature, relative humidity, or ambient concentration).

The size dependence of the corresponding growth processes is depicted in Figure 3. Diffusion-limited condensation appears to encourage the growth of smaller aerosols, whereas aerosol droplet reaction and equilibrium displacement favor the growth of larger aerosols; aerosol surface reactions yield a growth process that is intermediate between the other two growth processes. The processes that lead to growth/shrinkage of aerosols and that should be included in a regional aerosol model are presented in Table 1.

Since growth/shrinkage processes affect the aerosol size distribution, it is of interest to investigate how the coupling of growth and coagulation influence the aerosol size distribution. Figure 4 presents the results of 12-hour simulations of the initial aerosol size

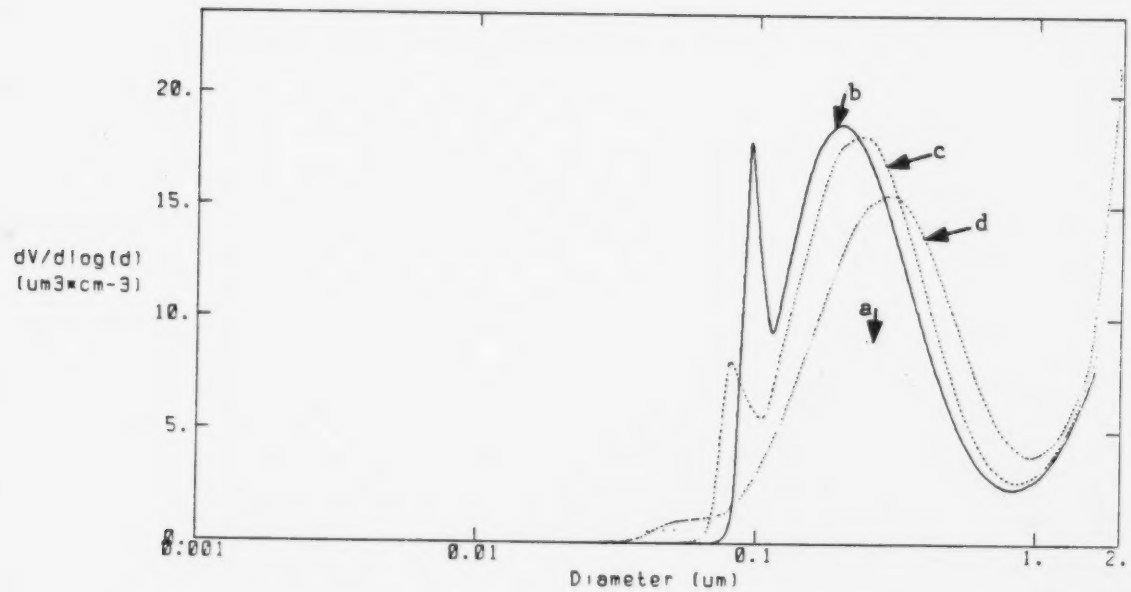

Fig. 3. Growth of an aerosol size distribution for various condensation processes. The amount of condensed material is 5.4 $\mu m^3/cm^{-3}$. Initial size distribution. Columbus, Ohio (Whitby, 1981b) (a = initial distribution; b = diffusion-limited; c = aerosol surface reaction; d = aerosol droplet reaction and equilibrium displacement). Simulations were performed with the CONFEMM model of Tsang and Brock (1983).

Table 1. Aerosol Growth/Shrinkage Processes of the Regional Aerosol Model

Growth/Shrinkage Law	Chemical Process*
Diffusion-limited condensation	Gas-phase formation of H_2SO_4 and condensible organics
Diffusion-limited evaporation	Evaporation of HCl†
Aerosol surface reactions	Oxidation of SO_2 to sulfate on carbon soot†
Aerosol droplet reactions	Oxidation of SO_2 to sulfate by O_2, H_2O_2 and O_3
Equilibrium displacement	Thermodynamic equilibrium of $HNO_3/NH_3/NH_4NO_3$ Deliquescence and hygroscopy of sulfate and nitrate ammonium salts Thermodynamic equilibrium of volatile organics† Change in aerosol density due to change in chemical composition

* The chemical processes are discussed in detail in the next section.

† These processes are not included in the regional model.

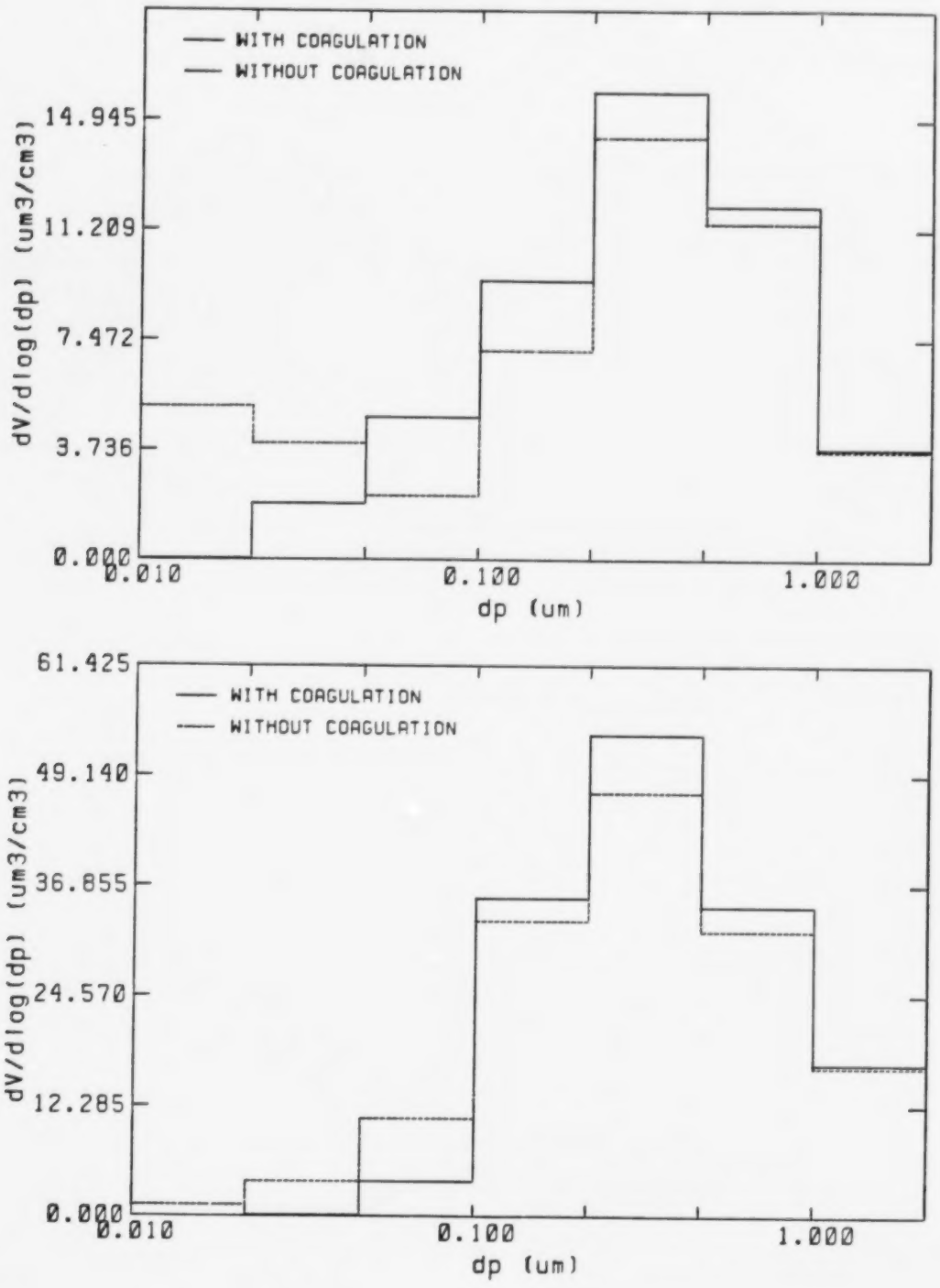

Fig. 4. Evolution of aerosol size distributions with condensation and with and without coagulation for hazy (top) and urban (bottom) conditions.

distributions presented in Figure 2, with diffusion-limited condensation of ammonium sulfate taking place at a rate of 5.4 $\mu m^3 cm^{-3}$/12 hours and 4.4 $\mu m^3 cm^{-3}$/12 hours for the hazy and urban case studies, respectively. The amount of aerosol volume produced during condensation corresponds to 50 and 10 percent of the initial aerosol volume for the hazy and urban cases, respectively. The simulations were performed with and without coagulation.

The results of the urban case study do not differ significantly from those presented in Figure 2 since the aerosol volume is not greatly affected by condensation. However, there are larger discrepancies between the cases with and without coagulation than there are in the cases presented in Figure 2, where no condensation occurs. This result is even more apparent in the hazy case, where condensation leads to a notable increase in aerosol volume. In this case, neglecting coagulation when condensation takes place strongly affects the aerosol size distribution: diffusion-limited condensation leads to the growth of smaller aerosols; if coagulation takes place, these smaller aerosols are scavenged by larger aerosols in the 0.1 to 1.0 μm diameter range; if coagulation is ignored, the concentration of small aerosols increases unrealistically. These results suggest that coagulation can be neglected in cases in which the aerosol volume is nearly constant; however, it is a critical process in the evolution of the aerosol size distribution when the aerosol volume increases due to gas-to-aerosol conversion. Coagulation should therefore be included in the simulation of regional aerosol dynamics.

Nucleation

Vapors that have a low vapor pressure, such as H_2SO_4, nucleate and form new aerosols. These new aerosols, whose size is of the order of 0.001 μm, grow quickly through coagulation with larger aerosols and condensation of additional vapor. Because the calculation of nucleation rates is sensitive to many parameters, these rates are rather uncertain. Also, the explicit treatment of nucleation requires modeling aerosols as small as of the order of 0.001 μm. Since aerosols smaller than 0.01 μm

are rarely measured, we opted for an alternative approach that calculates the rate of formation of new aerosols growing beyond a given size. This size will correspond in our model to the lower size range of the aerosol size spectrum. The monomer-balance theory of McMurry (1983) is well suited for this approach and is used in the regional aerosol model.

Removal Processes

Aerosols are removed from the atmosphere via sedimentation, dry deposition, and wet deposition. All these processes are strongly dependent on the size of the aerosol. Figure 5 presents the evolution of an aerosol size distribution that is affected by sedimentation, dry deposition, and washout below precipitating clouds. Aerosols may also be removed by rainout in clouds through nucleation of cloud droplets on aerosols and scavenging of aerosols through coagulation, thermophoresis, diffusiophoresis, and electrophoresis.

Sedimentation primarily removes large aerosols, i.e., those whose diameters are larger than 2 μm. Dry deposition, simulated according to Sehmel and Hodgson (1980), affects both smaller and larger aerosols and is ineffective in removing aerosols whose diameters range from 0.01 to 1.0 μm. Washout by precipitation below clouds was simulated according to Wang et al. (1978). This process also removes larger aerosols and does not scavenge aerosols in the 0.01 to 1.0 μm diameter range, the so-called Greenfield gap (Greenfield, 1957). These results are based on theoretical considerations, and it should be noted that, although qualitative agreement exists between experimental results and model calculations, some discrepancies still need to be resolved (Radke et al., 1980). The regional aerosol model incorporates the treatment of dry deposition and sedimentation. Dry deposition is treated according to the model of Sehmel and Hodgson (1980). Sedimentation is modeled with the Stokes formula (e.g., Friedlander, 1977). Currently, no treatment of wet deposition is considered.

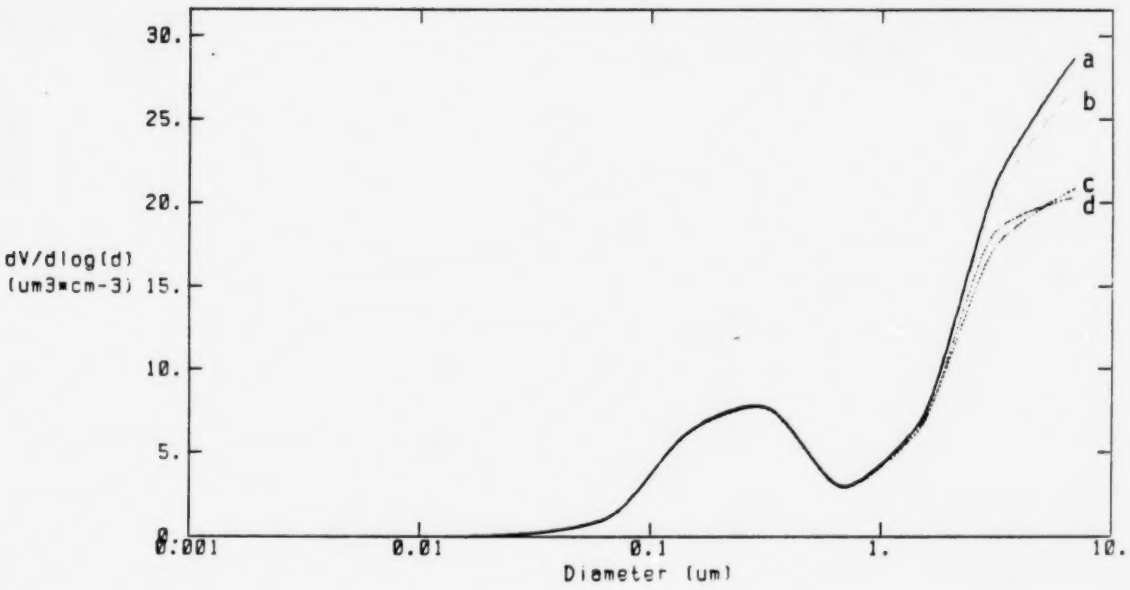

Fig. 5. Evolution of an aerosol size distribution undergoing removal by dry deposition, sedimentation, and washout by raindrops (a = initial distribution; b = sedimentation; c = wet deposition; d = dry deposition). Dry deposition and sedimentation were simulated for 12 hours under stable atmospheric conditions. The total aerosol removal used in simulating wet deposition was the same as that used for dry deposition.

AEROSOL CHEMISTRY

The chemical composition of an aerosol depends upon the condensation of gaseous species on the aerosol and on the chemical transformation of species in the aerosol phase. We review in this section the chemical reactions that lead to condensible species in the gas phase, chemical reactions that occur in the aerosol phase, and equilibrium thermodynamics of aerosols.

Gas-Phase Chemical Reactions

Condensible species that are considered in the regional aerosol model include H_2SO_4, HNO_3, NH_3, and some organic products. Ammonia will react with H_2SO_4 and HNO_3 to yield ammonium salts. The reaction of NH_3 with H_2SO_4 is fast and may be assumed to be irreversible (McMurry et al., 1983). The reaction of HNO_3 with NH_3 is reversible (Stelson et al., 1979) and is discussed in a later section on aerosol thermodynamics. The reaction of HCl with NH_3 yields NH_4Cl aerosols. However, this species is more elusive than are other ammonium salts and is not considered in our model.

The major reactions that lead to H_2SO_4, HNO_3, and condensible organic species are listed in Table 2. The reaction of SO_2 with OH is the major pathway for the formation of H_2SO_4. The oxidation of SO_2 by Criegee intermediates may be significant only at very low relative humidities. The formation of HNO_3 is believed to occur predominantly via the oxidation of NO_2 by OH during the day and by the chemistry of NO_3 radicals at night. However, the oxidation of NO_2 by OH may also take place at night since high nighttime concentrations of free radicals have been observed. For example, Stedman (1985) reported nighttime concentrations of free radicals

Table 2. Gas-Phase Reactions of Condensible Species

Reaction	Rate Parameter (ppm^{-1} min^{-1} and ppm^{-1})	Reference
$SO_2 + OH \rightarrow H_2SO_4 + HO_2$	1500	Atkinson and Lloyd, 1984
$NO_2 + OH \rightarrow HNO_3$	16000	Atkinson and Lloyd, 1984
$NO_2 + NO_3 \rightleftarrows N_2O_5$	1280	Atkinson and Lloyd, 1984
$N_2O_5 + H_2O \rightarrow 2HNO_3$	3.5×10^{-6} *	Tuazon et al., 1983
$PHEN^{\dagger} + NO_3 \rightarrow HNO_3 + PHO^{\dagger}$	15000	Atkinson and Lloyd, 1984
$FORM + NO_3 \rightarrow HNO_3 + HO_2 + CO$	0.93	Kerr and Calvert, 1984
$ALD2 + NO_3 \rightarrow HNO_3 + C_2O_3$	3.7	Kerr and Calvert, 1984
$ARO^{\dagger} + OH \rightarrow \alpha_1$ ORG	§	§
$OLE^{\dagger} + O_3 \rightarrow \alpha_2$ ORG	§	§
$OLE^{\dagger} + OH \rightarrow \alpha_3$ ORG	§	§

† Nomenclature of the Carbon-Bond Chemical Kinetic Mechanism:
PHEN = phenolic compound; PHO = phenoxy radical;
FORM = formaldehyde; ALD2 = other aldehydes;
C_2O_3 = peroxy radical; ARO = aromatic compound;
OLE = carbon-carbon double bond of olefins.

§ Rate parameters are to be determined.

* Rate parameter for the homogeneous reaction; this reaction may also take place heterogeneously at the aerosol surface.

of the order of 10^{-7} ppm. The OH radicals could result from the thermal decomposition of peroxyacetylnitrate in the presence of NO (Seigneur and Saxena, 1984). The hydrolysis of N_2O_5 occurs slowly in the gas-phase but may proceed at a faster rate if it takes place heterogeneously at the aerosol surface. Both processes are included in the model. The details of the chemistry of organic aerosol formation are still uncertain. It has been observed, however, that aromatics and long-chain olefins lead to secondary aerosol formation (e.g., Heisler and Friedlander, 1977; Grosjean, 1984; Franzblau et al., 1984; Fox et al., 1984). These reactions are cast in the lumped form of the precursor being oxidized to a condensible product. No mechanistic details are included since they are still unknown. The stoichiometric coefficients will be defined from the results of smog chamber experiments.

Aerosol-Phase Chemical Reactions

The formation of nitrate in liquid droplets occurs too slowly to be of significance (Schwartz and White, 1983; Seigneur and Saxena, 1984). The formation of sulfate may occur at an appreciable rate in liquid droplets and is therefore likely to occur in liquid-coated aerosols. Atmospheric measurements of aerosol growth suggest the existence of such reactions (McMurry and Wilson, 1982, 1983; Gillani and Wilson, 1983). These reactions include the oxidation of SO_2 by O_2 catalyzed with trace metals, by H_2O_2 and by O_3. Preliminary calculations suggest that the oxidation of SO_2 by O_3 is too slow to be significant in liquid aerosols because the pH of the liquid film coating an aerosol is generally below 3, and the oxidation of SO_2 by O_3 is slow at these low pH values. The oxidation of SO_2 by H_2O_2 occurs at a notable rate at low pH values, and it is a major oxidation pathway for SO_2 in fog and cloud droplets. However, since the amount of water contained in aerosols is typically 1000 times less than that present in fog or clouds, the oxidation of SO_2 by H_2O_2 occurs at a slow rate--of the order of 0.1 percent per hour. The oxidation of SO_2 by trace metals may be the major pathway; the kinetics of this pathway becomes slower as the pH decreases; however, trace metal concentrations tend to increase as the liquid water content decreases and

will therefore maintain a faster kinetics than the reactions that involve O_3 and H_2O_2.

Aerosol Thermodynamics. Several chemical species are present in both the aerosol and gas phases. The relative distribution of these species between the two phases is governed by equilibrium thermodynamics although diffusion kinetics may also contribute to the partition of a species between the two phases. In the regional aerosol model, it is assumed that chemical species are at thermodynamic equilibrium between the aerosol phase and the gas phase, and within the aerosol phase.

Inorganic species that are considered in the aerosol thermodynamic model include ammonium salts of sulfate and nitrate. These chemical species have been measured in atmospheric aerosols (e.g., Gaarenstroom et al., 1977; Lewis and Macias, 1980; Wolff et al., 1983; Harrison and Sturges, 1984) and are generally present in the fine aerosol range, i.e., in aerosols whose diameters are smaller than 2 μm. These aerosols result from the reactions of H_2SO_4 and HNO_3 with NH_3, as discussed previously.

Certain other sulfate and nitrate species have been measured in atmospheric aerosols that result from the displacement of other aerosol constituents. For example, HCl may be displaced from NaCl in marine aerosols by H_2SO_4 and HNO_3 (Harrison and Pio, 1983) to produce the salts Na_2SO_4 and $NaNO_3$. Similarly, $CaCO_3$ may react with H_2SO_4 to produce $CaSO_4$ and gaseous CO_2, and PbBrCl may be converted by reaction with H_2SO_4 to $PbSO_4$ and gaseous HCl and HBr. These species are not included in the aerosol thermodynamic model since quantitative descriptions of their thermodynamics have not yet been developed.

Another inorganic salt that has been observed in fine aerosols is NH_4Cl, which results from the reaction of NH_3 with HCl. This compound could eventually be included in the aerosol thermodynamic model; however, since its presence in aerosols is generally much less important than that of sulfate and nitrate ammonium salts and appears to be significant only near large sources of Cl_2 and HCl, it is not included in the model.

Several models of aerosol thermodynamics have been developed (Saxena et al., 1983; Bassett and Seinfeld, 1983, 1984; Saxena, 1984). The major characteristics of the behavior of atmospheric sulfate/nitrate/ammonium aerosols may be summarized as follows:

Sulfuric acid is much less volatile than is nitric acid. Since ammonia neutralizes the former preferentially, ammonium sulfate aerosols are formed first. As the ammonia concentration increases from 0 to more than twice the sulfuric acid concentration, the following aerosols are formed:

$$[NH_3]_T^* = 0, \qquad H_2SO_4(\ell)$$

$$0 < [NH_3]_T < [H_2SO_4], \qquad H_2SO_4(\ell),\ NH_4HSO_4(s, \ell)$$

$$[H_2SO_4] < [NH_3]_T < 1.5[H_2SO_4], \qquad NH_4HSO_4(s, \ell),\ (NH_4)_3H(SO_4)_2(s, \ell)$$

$$1.5[H_2SO_4] < [NH_3]_T < 2[H_2SO_4], \qquad (NH_4)_3H(SO_4)_2(s, \ell),\ (NH_4)_2SO_4(s, \ell)$$

$$0 < [NH_3]_T - 2[H_2SO_4] < \frac{K_{AN}}{[HNO_3]}, \qquad (NH_4)_2SO_4(s, \ell)$$

$$\frac{K_{AN}}{[HNO_3]} < [NH_3]_T - 2[H_2SO_4], \qquad (NH_4)_2SO_4(s, \ell),\ NH_4NO_3(s, \ell),$$

$$(NH_4)_2SO_4 \cdot 2NH_4NO_3(s),\ (NH_4)_2SO_4 \cdot 3NH_4NO_3(s)$$

The equilibrium constant K_{AN} for ammonium nitrate is a function of the relative humidity, temperature, and aerosol pH (Stelson and Seinfeld, 1982a,

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* $[NH_3]_T$ represents the total ammonia concentration prior to neutralization of H_2SO_4 and HNO_3.

1982b). Ammonium nitrate aerosols are formed when the product of the gas-phase concentrations of NH_3 and HNO_3 exceeds the saturation equilibrium constant K_{AN}.

The aerosol species listed above may be present in a liquid or solid phase. If these species are present in a liquid phase, the ionic species H^+, HSO_4^-, SO_4^{2-}, NO_3^-, and NH_4^+ will result from the ionization of the aerosol salts. It should be noted that if the species are present in a liquid phase, a minute amount of HNO_3 will dissolve, and nitrate will be present in the aerosol.

The existence of a liquid film around the aerosol depends primarily on the deliquescent properties of the aerosol. At an ambient temperature of 25`C, the following relative humidities of deliquescence will determine the state of the aerosol:

Aerosol Species	Relative Humidity of Deliquescence
H_2SO_4	Always liquid
NH_4HSO_4	40 percent
$(NH_4)_3H(SO_4)_2$	69 percent
$(NH_4)_2SO_4$	80 percent
NH_4NO_3	62 percent

A given salt may be present in the solid phase above its relative humidity of deliquescence if its saturation product in the liquid phase is exceeded. For example, the following relationships are defined for ammonium sulfate and nitrate (Saxena et al., 1983).

$$[NH_4^+]^2\ [SO_4^{2-}] < 1.05\ mol^3 \cdot kg^{-3}$$

$$[NH_4^+]\ [NO_3^-] < 13.06\ mol^2 \cdot kg^{-2}$$

Above their relative humidities of deliquescence, sulfate and nitrate aerosols are hygroscopic that is, the amount of associated condensed water increases as relative humidity increases.

MATHEMATICAL MODELS OF ATMOSPHERIC AEROSOLS

A model that describes the evolution of the aerosol concentration, size distribution, and chemical composition in a grid cell of a 3-D regional model must treat aerosol dynamics (i.e., coagulation, growth, and shrinkage), thermodynamics (i.e., equilibrium of sulfate, nitrate, and ammonium species), and chemical kinetics (i.e., gaseous, heterogeneous, and aqueous). Emission, transport, and removal processes are included as inter-grid-cell processes in the regional model and are therefore not discussed further here. A mathematical model of aerosol dynamics, thermodynamics, and chemical kinetics does not currently exist. However, individual models that describe the dynamics, thermodynamics, or kinetics of aerosols do exist. We have discussed mechanisms for the chemical kinetics of aerosol species formation in the previous section. In this section we focus on the selection of models of aerosol dynamics and thermodynamics.

Because of the computational requirements of a regional-scale simulation, it is imperative to develop an aerosol model that offers a reasonably accurate solution and is computationally efficient. To that end, we reviewed several mathematical models of aerosol dynamics and thermodynamics of various degrees of sophistication. This section presents an overview of these mathematical models and general discussions of their comparative accuracies and computational requirements.

Aerosol Dynamics Models

In solving the mathematical equations of aerosol system dynamics, most difficulties are associated with the solution of the coagulation and condensation/evaporation terms. The coagulation term consists of an integro-differential equation, and the condensation/evaporation term consists of a

hyperbolic differential equation. Three major approaches have been developed to simulate aerosol dynamics. These approaches differ primarily in their representation of the size distribution of aerosols--continuous, discrete, and parameterized. Examples of an aerosol size distribution modeled with continuous, discrete, and parameterized lognormal representations are presented in Figure 6.

The first approach, based on a continuous representation of the aerosol size distribution, involves finding the exact solution of the mathematical equations using numerical techniques for the evaluation of integrals. This approach requires the use of an accurate numerical technique and may therefore be computationally expensive. In our study, this approach is characterized by the COAGUL model for the simulation of coagulation (Suck and Brock, 1979) and the CONFEMM model for the simulation of condensation (Tsang and Brock, 1982).

In the second approach, a discrete approximation is made to the continuous representation of the aerosol size distribution. The accuracy of the solution and the corresponding computational costs depend, therefore, on the resolution of the discrete approximation. As the discrete approximation tends toward the continuous representation, the solution of this approach tends toward the exact solution. This approach is characterized by the ESMAP model for the simulation of coagulation and condensation (Warren and Seinfeld, 1984).

The third approach assumes a known form of the mathematical representation of the aerosol size distribution, and thus the solution of the dynamic equation involves the calculation of the parameters of this mathematical expression. This approach is represented by the AGRO model (Whitby, 1981a; Whitby and McMurry, 1984), which assumes lognormal distributions of the nuclei, accumulation, and coarse aerosol modes.

Of these three methods, the first approach yields the most accurate results. The third approach, because of its parameterization, provides less accurate results. The accuracy of the second approach depends on the resolution of the discrete approximation. Conversely, the computational cost of the

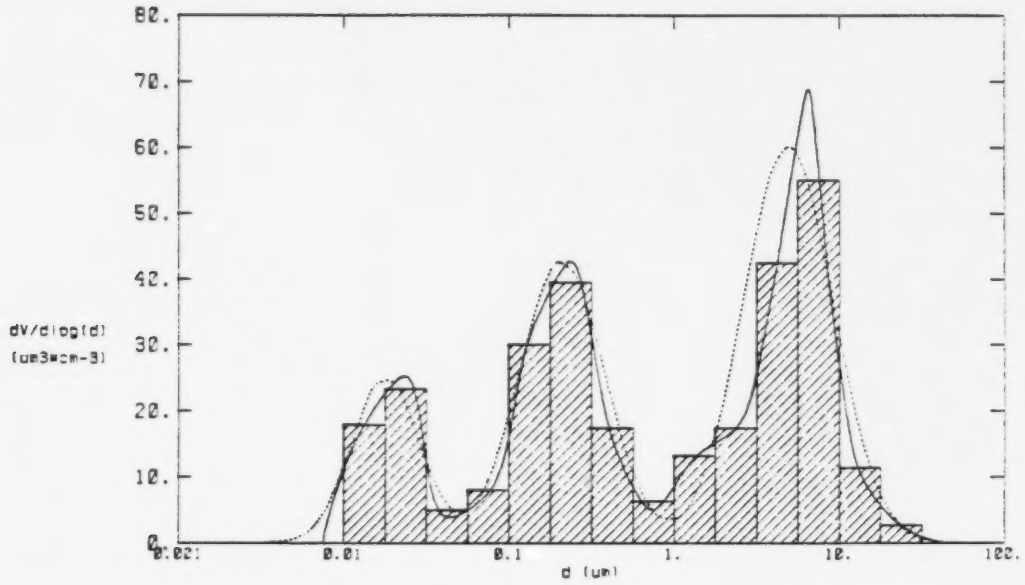

Fig. 6. Representation of an aerosol size distribution with a continuous representation (———), lognormal modal representation (·····) and sectional representation (▨) --background size distribution. 29 October 1975, General Motors Sulfate Study. Source: (Whitby, 1978).

numerical solution is highest for the first approach and lowest for the third approach. Both accuracy and computational cost need to be taken into account in modeling aerosol dynamics at the regional scale.

The solution of a continuous representation of the aerosol size distribution is actually obtained by a numerical solution that approximates the size distribution of a finite number of points. Comparisons with analytical solutions suggest that 40 points can accurately represent the size distribution of aerosols whose diameters range from 0.001 to 10 μm. For coagulation, quadrature with spline functions and solution of a set of ordinary differential equations are carried out. For condensation, a finite element method that minimizes numerical dispersion and diffusion is used.

The solution of the discrete, or sectional, representation of the aerosol size distribution is obtained by solving a set of ordinary differential equations. No quadrature is needed for the integration of the coagulation equation since it has already been performed in the calculation of the sectional coagulation coefficients. Solution of the condensation equation may involve some numerical diffusion because of the sectional representation. The number of differential equations to be solved depends on the resolution of the sectional representation.

The solution of the parameterized representation requires the solution of four ordinary differential equations for the total number and volume of the nuclei and accumulation modes, respectively. No quadrature is needed since it is implicitly included in the definition of the parameterized coagulation coefficients of aerosol dynamics.

The AGRO, ESMAP (with 12 and 39 sections), COAGUL and CONFEMM models were applied to the simulation of coagulation and condensation for atmospheric concentrations typical of clear, hazy, and urban conditions. Simulations were conducted for 12 hours for aerosols in the size range 0.001 to 10 μm. Condensation was treated as a diffusion-limited condensation of ammonium sulfate. Condensation amounted to 0.3, 5.4, and 4.4 $\mu m^3 cm^{-3}$ for clear, hazy, and urban conditions, respectively. A summary of the mathematical models is

given in Table 3. The results of the model simulations are presented in Table 4. Figure 7 presents the aerosol size distribution calculated after 12 hours of simulation with coagulation and condensation for hazy conditions.

In this model comparison, the COAGUL and CONFEMM models were taken as reference since they are based on accurate numerical solutions of the continuous number distribution equation.

The results presented in Table 4 and Figure 7 indicate that the ESMAP model, with either 39 or 12 sections, accurately simulates coagulation. Because the AGRO model assumes a constant standard deviation for the lognormal distributions, it is much less accurate, particularly for urban conditions. The ESMAP and COAGUL models show that the standard deviation actually decreases as coagulation takes place. The AGRO model is being improved to include a time-dependent standard deviation.

The ESMAP model simulates condensation less accurately than it simulates coagulation because of numerical diffusion resulting from the sectional representation. The performance of the AGRO model is reasonable, considering its lower computational requirements. It should be noted that the computational requirements of the AGRO model are about 50 times less than those of the COAGUL and CONFEMM models. The computational requirements of the ESMAP model, which lie between those of the AGRO model and those of the COAGUL and CONFEMM models, depend on the number of sections used to represent the aerosol size distribution. A more detailed comparison of these aerosol dynamics models awaits the development of a final version of the AGRO model and will be reported later.

Aerosol Thermodynamics Models

Models of aerosol thermodynamics considered in this review simulate the thermodynamic equilibrium of sulfate/nitrate/ammonium aerosols. These models include the KEQUIL (Bassett and Seinfeld, 1984), EQUIL (Bassett and Seinfeld, 1983), and MARS (Saxena, 1984) models. These models calculate the amount of sulfate, nitrate, ammonium, and water present in the aerosol as a function of

Table 3. Summary of Mathematical Models for Simulation of Aerosol Dynamics in the Size Range 0.001 to 10 μm.

Dynamic Equation	Number of Differential Equations Solved	Model	
		Coagulation	Condensation
Continuous	40	COAGUL	CONFEMM
Sectional	39	ESMAP	ESMAP
	12	ESMAP	ESMAP
Parameterized	4	AGRO	AGRO

Table 4. Preliminary Comparison of Model Simulation Results

Coagulation				Condensation			
Model	Average Percentage Difference			Model	Average Percentage Difference		
	Clear	Hazy	Urban		Clear	Hazy	Urban
COAGUL	(Reference)			CONFEMM	(Reference)		
ESMAP (39 sections)	1%	2%	7%	ESMAP (39 sections)	9%	12%	3%
ESMAP (12 sections)	3%	9%	10%	ESMAP (12 sections)	18%	35%	10%
AGRO	3%	6%	39%	AGRO	19%	37%	13%

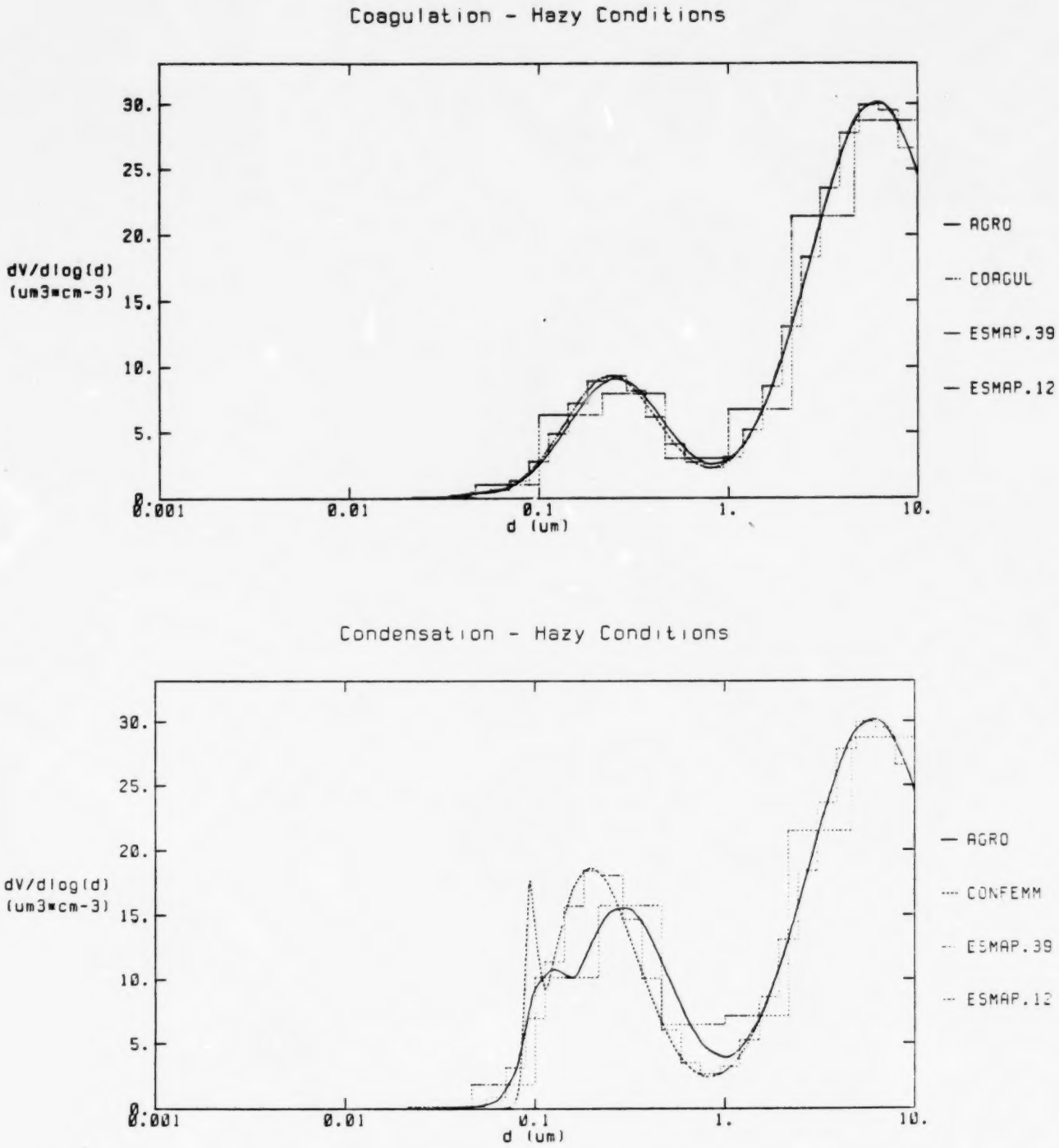

Fig. 7. Simulation of the evolution of an aerosol size distribution undergoing coagulation (top) and condensation (bottom).

the gas-phase concentrations of sulfuric acid, nitric acid, and ammonia, previous sulfate, nitrate, and ammonium aerosol concentrations, relative humidity, and temperature. These calculations are based upon basic thermodynamic principles.

The KEQUIL model provides an accurate solution of the thermodynamic equations including the Kelvin effect, i.e., the effect of aerosol size on the aerosol chemical composition. The EQUIL model is based on the same thermodynamic equations as is the KEQUIL model but assumes that the aerosol chemical composition is independent of size. The MARS model was developed to provide a computationally less demanding yet fairly accurate solution of the thermodynamic equilibrium problem. It includes several assumptions regarding the aerosol chemical composition that allow reduction of the number of thermodynamic equilibrium relationships considered. Comparison of these models is being carried out and will be reported later.

Formulation of the Aerosol Model

The aerosol model developed for regional applications will require good predictive accuracy as well as reasonable computational costs. For these reasons, we selected a sectional representation of the aerosol size distribution between 0.01 and 10 μm. Seven size sections are included between 0.01 and 2.5 μm (fine aerosol range). Two sections constitute the coarse aerosol range from 2.5 to 10 μm. Aerosols in the fine range undergo coagulation, growth/shrinkage, new aerosol formation at 0.01 μm, thermodynamic equilibrium, aerosol chemical reactions, and dry deposition. Aerosols in the coarse aerosol range undergo dry deposition and sedimentation. All aerosol size ranges are also affected by emissions and atmospheric transport. The thermodynamics of the aerosols are treated with the MARS model. A typical aerosol population calculated by the model is presented in Figure 8.

CONCLUSION

We have reviewed the physical and chemical processes that affect the concentration, size distribution, and chemical composition of atmospheric

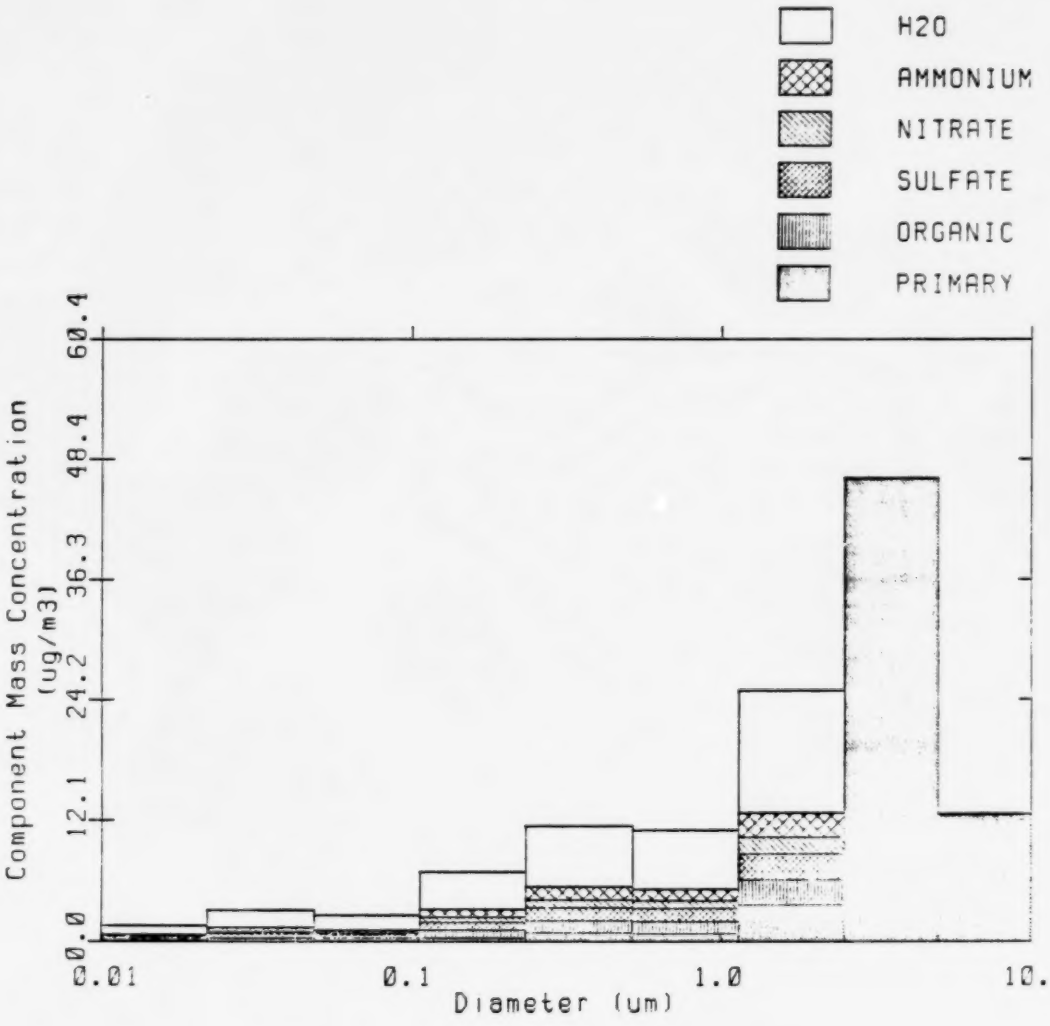

Fig. 8. Example of the concentration and chemical composition of a size-distributed aerosol calculated by the regional aerosol model.

aerosols at the regional scale. Physical processes include coagulation, growth or shrinkage of the aerosols due to condensation or evaporation, nucleation of new aerosols, sedimentation, and dry and wet deposition. Chemical processes include thermodynamic equilibrium between the gas and aerosol phases and within the aerosol phase, gas-phase chemical reactions leading to condensible vapor, and aerosol-phase chemical reactions.

Our present model for regional aerosols treats aerosols that consist of a nonvolatile solid core, sulfate, nitrate, ammonium, and organic species. The chemical composition is assumed to be independent of the aerosol size. The size distribution is approximated with a sectional representation. This approach was shown to be fairly accurate when compared with more accurate models.

Further work will involve incorporating this model of aerosol dynamics and chemistry in the EPA regional model, some treatment of aerosols in clouds, and the evaluation of this regional aerosol model with field data.

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